

# Oil pollution and drinking water odour

## Introduction

During the World Congress on Sea-Pollution, held in Rome in december 1970, a severe warning was given to the world concerning the high pollution with oil and pesticides of seas like the North Sea.

Water pollution by oil not only has disastrous consequences for birds and aquatic life, but some oil components are also toxic to human and animal life or consist of organic substances with a very intense odour.

The contamination by oil products of the river Rhine, being a serious problem in relation to the taste and odour of drinking water, was recently discussed at a meeting of the IAWR\*) (Zürich, 22-24 october 1970) (Van Puffelen, 1970).

The known quantity of crude oil available on earth is valued at approximately 100 milliard tons. The yearly world consumption of oil, now about 1.5 milliard tons, is increasing very rapidly. It has tripled during the period 1950-1967 (Van Soest, 1970). As even relative small quantities of oil products may spoil the taste and odour of water, the steadily growing use of oil products means an increasing threat of contamination of water resources. Whereas in most cases the contamination of groundwater is accidental and very local, the surface waters of the Netherlands, like the river Rhine and Meuse and the North Sea are continuously polluted by oil.

It was estimated (Biemond, 1966) that in 1964 a total quantity of 20.000 tons of oil was discharged by the Rhine and there are no indications that the pollution was considerably less during 1970. More than half of the reported accidents on the river are related to oil spillage. The concentration of oil in the Rhine usually varies between 0.01-1.0 mg/l (Biemond, 1966; Meijers, 1970; Rijkswaterstaat, 1968). This means that in general the extractable organic pollutants in Rhinewater consist for the greater part of oil products.

In spite of the strong efforts to reduce oil spillage during the production, transportation, storage and consumption processes (Blokker, Liedmeier, 1968) the problem of water pollution by oil is not likely to diminish; on the contrary it will become more serious because of the rapid growth of oil consumption in the near future.

The future drinking water supply of the Netherlands mainly depends on surface water resources. In this connection a study has been started on the influence of oil products on the taste and odour of drinking water.

The degree in which an odorous compound is objectionable to the drinking water supply, depends on the odour intensity of the compound and its persistence. Very persistent odour compounds can be characterized by a low volatility and a small biodegradability (Zoeteman, 1970). The odour substances in surface water that might origi-

nate from pollution by oil can be divided into three main categories:

- constituents of the discharged oil;
- intermediates of the biological or chemical oxidation of the oil compounds;
- products synthesized during the microbiological mineralization of the oil.

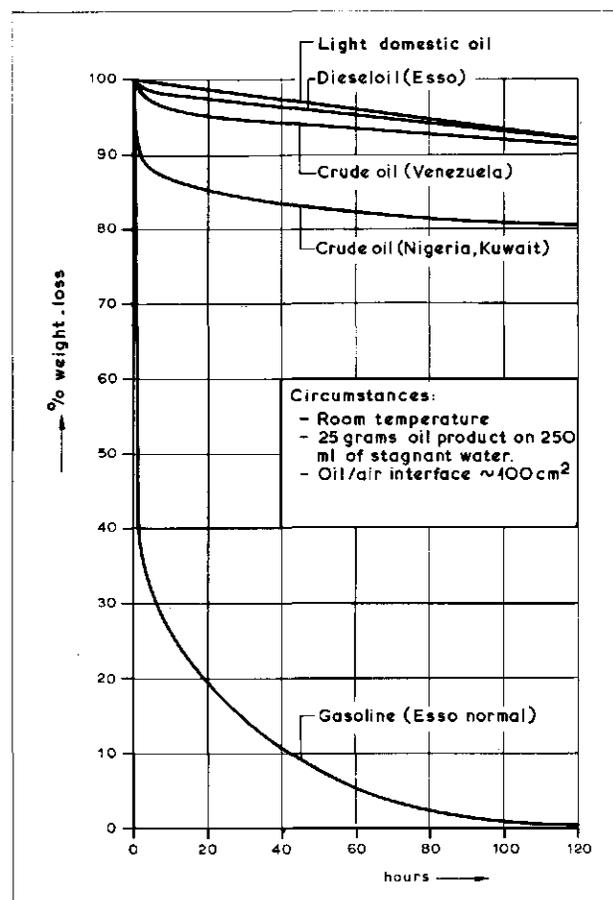
Some organic odour compounds, belonging to one of these three categories, will be discussed in this paper. The category to which an odour compound belongs determines to a certain extent the abatement of the contamination of the water.

## Physical changes of oil in water

After an accidental pollution of the river with large quantities of hundreds of tons of crude oil or gasoil the oil film on the water surface generally lasts for only a relatively short periode of 10-50 hours. The oil film disappears because oil compounds evaporate, dissolve in the water or are emulsified.

The aromatic hydrocarbons are generally more water-soluble than the paraffinic ones.

Figure 1 - Weight-loss of oil products by evaporation.



\*) Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet.

Figure 1 gives an impression of the weight-loss by evaporation of several crude oils and oil products at room temperature. In the river evaporation of crude oil fractions and diesel oil fractions takes place on a relatively small scale. In the North Sea however this process causes an important reduction of the quantities of spilled oil because the oil remains there much longer. Finally, the high boiling, waterinsoluble compounds of oil will accumulate. They can still contaminate the water in emulsified form.

Figure 2 shows the relatively high concentration of about 1 ppm of the high boiling persistent oil fraction in the seawater, as found near the Dutch coast of Scheveningen during a period of stormy weather (23rd October 1970). Especially the dissolved and emulsified oil fractions can bring on odour problems during the purification and distribution of drinking water, either by their actual presence as odour compounds or by their possible influence on odour production during the biological degradation.

#### Odour compounds of oil products

Crude oils and oil products not only consist of paraffinic and aromatic hydrocarbons but also of minor quantities of nitrogen and sulfur compounds. Especially the sulfur compounds can have a very intense odour.

Table I gives the threshold odour concentration (TOC) of several crude oils and oil products in water. The values in the left column have been determined in water of 15° C in our laboratory by a panel of 5 persons.

TABLE I - TOC values of several crude oils and oil products

Product	TOC (ppm)	TOC from literature (ppm)
<i>Crude oils</i>		
Aramco (Arabia)		0.06*
Kuwait (Kuwait)	0.01	0.35**
Kirkuk (Iraq)	0.001	
Qatar (Qatar)		0.04*
Essider (Libya)		0.03*
Nigerian-Light (Nigeria)	0.0005	
Cabimas (Venezuela)	0.05	
<i>Oil products</i>		
Normal gasoline (Esso)	0.01	
Extra gasoline (Esso)	0.01	
Diesel fuel (Esso)	0.0005	0.0005**
Light domestic oil (Shell)	0.005	
Medium domestic oil (Shell)	0.5	
Fuel oil 400 (Shell)	0.002	
Fuel oil 800 (Shell)	0.1	
Fuel oil 3500 (Shell)	0.1	

\*) Sontheimer, Kölle (1967).

\*\*) Holluta (1961).

This table shows that contamination of Rhine water with oil can already directly cause severe odour problems within the concentration range of 0.01-1.0 ppm.

To gain a better insight into the nature of the compounds that are responsible for the odour of oil products the TOC of several hydrocarbons was estimated (table II). From this table it can be concluded that some substituted aromates like styrene and tert. buthylbenzene are important, and even more so are polycyclic aromates like indene and the naphthalenes.

Column : SE 30  
Injection : 4 µl  
Detection : F.I.D.  
Temp. prog.: 150-275°C (12°/min.)

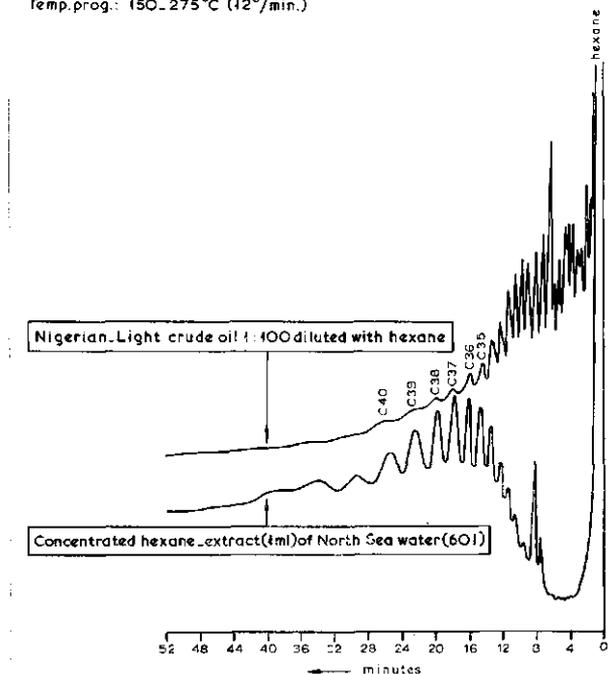


Figure 2 - Gaschromatograms of persistent oil residue in North Sea at Scheveningen and a crude oil.

Apart from these aromatic hydrocarbons sulfur compounds like diphenyldisulfide (TOC = 0.005 ppm (Brady, 1968)) play an essential role in the odour of oil products. When the human nose is used as a detector in gaschromatographic analysis of mineral oils, it was found that these sulfur- and aromatic compounds were indeed main-

TABLE II - Order of magnitude of TOC of some hydrocarbons in water

Paraffines	TOC ppm	Aromates	TOC ppm
<i>n-alkanes</i>		<i>n-alkylbenzenes</i>	
n-heptane	50	benzene	10
n-octane	10	toluene	1
n-nonane	10	ethylbenzene	0.1
n-decane	10	n-buthylbenzene	0.1
n-undecane	10	<i>benzenes (miscellaneous)</i>	
n-dodecane	10	styrene	0.05
<i>branched alkanes</i>		o/m/p-xylene	1
2-methylheptane	50	cumene	0.1
2-methylnonane	10	1, 3, 5/1, 2, 4 trimethyl-	
2-methylundecane	10	benzene	0.5
3-methylhexane	500	tert. buthylbenzene	0.05
3-methyloctane	100	p-cymene	0.1
2,2-dimethylpentane	100	<i>polycyclicaromates</i>	
2,2-dimethylheptane	50	tetrafin	0.01 *)
		indene	0.001
		naphthalene	0.005
		2,6-dimethylnaphthalene	0.01**)
		2,6-dimethylantracene	0.5**)

\*) Rosen c.s. (1963).

\*\*) Brady (1968).

ly responsible for the odour of water contaminated with oil.

The contribution of each compound to the total odour intensity was estimated by diluting the sample with hexane till the majority of the testing panel could no longer detect the smell of the odour substance.

Figure 3 gives the dilution factor till the threshold level of the odour compounds of three oil products. The character of the most intense odours is also given in this figure. These „odourchromatograms” clearly show the substantial contribution of naphtenic and sulfur compounds to the odour of the heavier oil products.

#### Odour compounds as intermediates of the (bio)chemical oxidative mineralization of oil

The biological oxidation of oil proceeds considerably faster than the chemical one within the temperature range of 0-25° C, which is important for the drinking water supply. In case of chemical oxidation of oil the products can have an intense odour and their influence will depend on their biodegradability. Generally an initial chemical oxidation of hydrocarbons opens the way to biodegradation. For this reason only the accumulating intermediates of the biological oxidation of oil will be considered.

Hydrocarbons that can be biodegraded very easily are the linear paraffins up to C-22 and the non-substituted aromates like naphtalene. Saturated ringsystems and strongly branched paraffins or aromates belong to the hydrocarbons with a high resistance to microbial oxidation.

The generally accepted oxidative degradation pathway of linear paraffins with more than 8 carbon atoms proceeds as shown schematically in figure 4 (Mason, 1957; Baptist-Coon, 1959-1960; Foster, 1962; Azoulay-Heydeman, 1963).

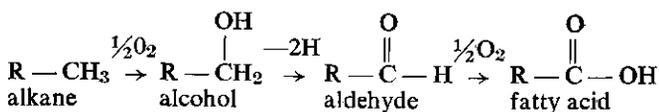


Figure 4 - First steps in the biodegradation of alkanes.

The formed fatty acid is degraded by the wellknown  $\beta$ -oxidation via acetic acid to carbondioxide and water. The biodegradability of hydrocarbon chains decreases with increasing branching and length of the side chains as was shown by studies of Thijsse-v. d. Linden (1961), V. d. Linden-Thijsse (1965) and Ooyama-Foster (1965). Also the place of the substitution is important for the oxidation velocity of intermediate oxidation products. Intermediate  $\beta$ -methyl substituted fatty acids like isovaleric acid are oxidized much easier than  $\alpha$ -methyl fatty acids like trimethylacetic acid (pivalic acid). These results were confirmed by a study of Mohanrao and McKinney (1962) on the utilization of quaternary carbon compounds by microbial sludges.

In case the hydrocarbons have a high resistance to microbial oxidation „co-oxidation” can occur, which results in the accumulation of oxidation products like alcohols and ketones. Ooyama and Foster (1965) studied this co-oxidation of non-growth hydrocarbons on saturated cyclic hydrocarbons like methylcyclopentane. The production of ketones is found in experiments with simple hydrocarbons (Lukins, 1962), which have little significance for the drinking water supply because of their high volatility.

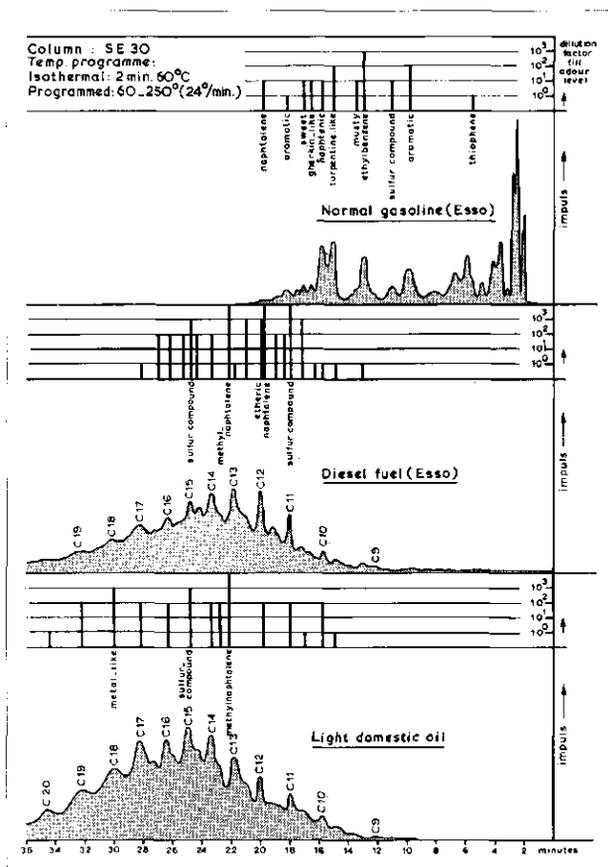


Figure 3 - Odourchromatograms of oil products.

Till now the influence of the co-oxidation of high boiling compounds on the odour of water has not been studied. However, as a rule, the quantities of these products that will be formed during bacterial growth on spilled oil in water are very small.

Aromatic hydrocarbons can be oxidated by different mechanisms. Figure 5 gives a simplified scheme of the degradation of unsubstituted aromates and alkylbenzenes with odd-numbered side chains (V. d. Linden-Thijsse, 1965).

The degradation of alkylbenzenes with even-numbered side chains proceeds via phenylacetic acid. This acid is subsequently hydroxylated after which acetoacetic acid and smaller compounds result from the ring-splitting reaction.

The character of the intermediate oxidation products of the dissimilative metabolism of aromatic hydrocarbons generally does not point out possible odour problems because of the low volatility and odour intensity of these intermediates. A relatively very volatile intermediate like phenol has already a TOC of 10 ppm (Bucksteeg-Dietz, 1957). In all these TOC determinations however, the sensitivity of the tester plays an important role (Baker, 1963).

From the above it can be concluded that accumulating intermediate oxidation products of branched paraffins might cause odour problems. Theoretically especially the  $\alpha$ -substituted fatty acids can accumulate. The role of these acids must be considered more in detail.

An  $\alpha$ -substituted fatty acid like trimethylacetic acid can accumulate during the microbial oxidation of 2,2-dimethylalkanes as illustrated in figure 6.

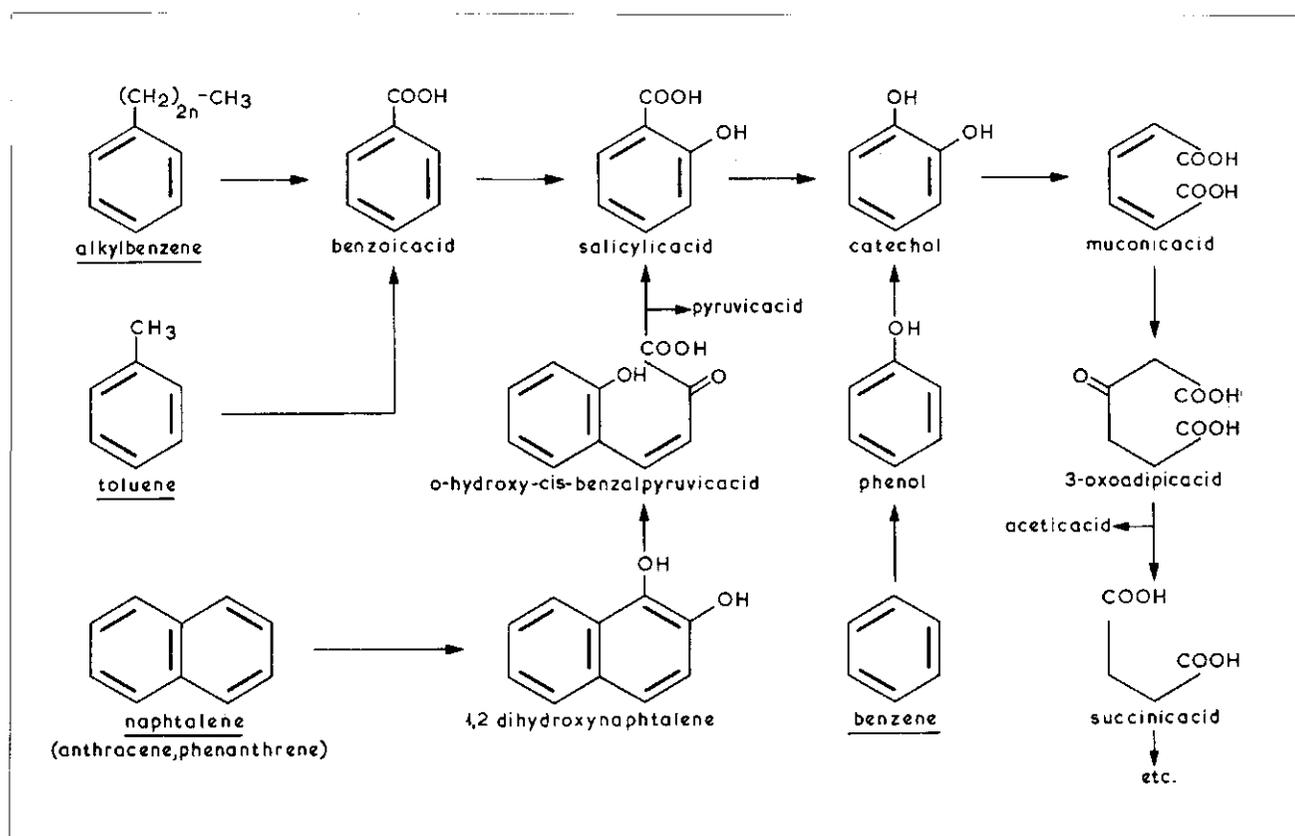


Figure 5 - Supposed simplified degradation pathways of unsubstituted aromates and alkylbenzenes with odd-numbered side chains.

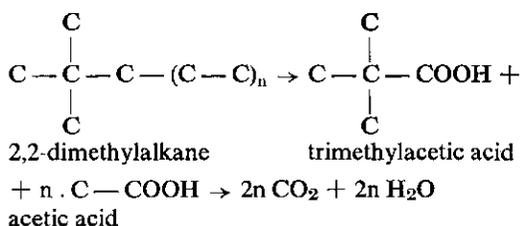


Figure 6 - Possible accumulation of trimethylacetic acid from substituted alkane degradation.

Other  $\alpha$ -substituted fatty acids like isobutyric acid and 2-methylbutyric acid can result from the breakdown of the corresponding isoparaffins. The role of these fatty acids as odour compounds in water will depend on their threshold odour concentration.

The TOC of the lower fatty acids, as given in table III, does not indicate a very high odour intensity of the intermediate fatty acids. Considering the phenomenon of odour synergism that can intensify the odour problems

TABLE III - TOC of lower fatty acids

Fatty acid	TOC (ppm)
formic acid	8000
acetic acid	200
propionic acid	200
butyric acid	40
isobutyric acid	30
valeric acid	10
isovaleric acid	5
2-methylbutyric acid	40
trimethylacetic acid	50
2-ethylbutyric acid	10

(Rosen, Skeel, Ettinger, 1963), the intermediates might influence the odour of the water at concentrations that are several times lower than their TOC's.

As the oil content of the water in the Rhine usually does not exceed a level of 1 ppm it can safely be stated that relative high quantities of the isoparaffins have to be converted into the corresponding iso-fatty acids before odour problems can result from it. For this reason the accumulation of  $\alpha$ -methyl fatty acids from microbial oxidation of isoparaffins was examined.

A hydrocarbon utilizing *Pseudomonas* strain and an *Achromobacter* strain were grown during 3 weeks at room temperature on resp. 2-methylheptane, 2-methylnonane, 2-methylundecane and 2,2-dimethylheptane. The culture medium consisted of ammoniumnitrate (1 g/l), dipotassiumphosphate (0.5 g/l) and tapwater to which 4 ml/l of the hydrocarbon was added after sterilization. The culture flasks of 1000 ml were filled with 100 ml medium and were closed air-tightly to prevent evaporation of volatile compounds. After incubation on a shaker the remaining hydrocarbon was removed by pentane extraction after addition of sodium hydroxide. Subsequently the medium was acidified and the present fatty acids were extracted with dichloromethane. This extract was concentrated and analyzed by gaschromatography. Figure 7 shows the results for the *Pseudomonas* strain after growth on 2-methylundecane and 2,2-dimethylheptane. During all experiments only trace amounts of the isoparaffins were converted into the corresponding iso-fatty acids. This indicates that once the degradation of branched hydrocarbons has started this mainly results in a complete oxidation to carbon dioxide and water. Therefore a considerable effect on the odour of drinking

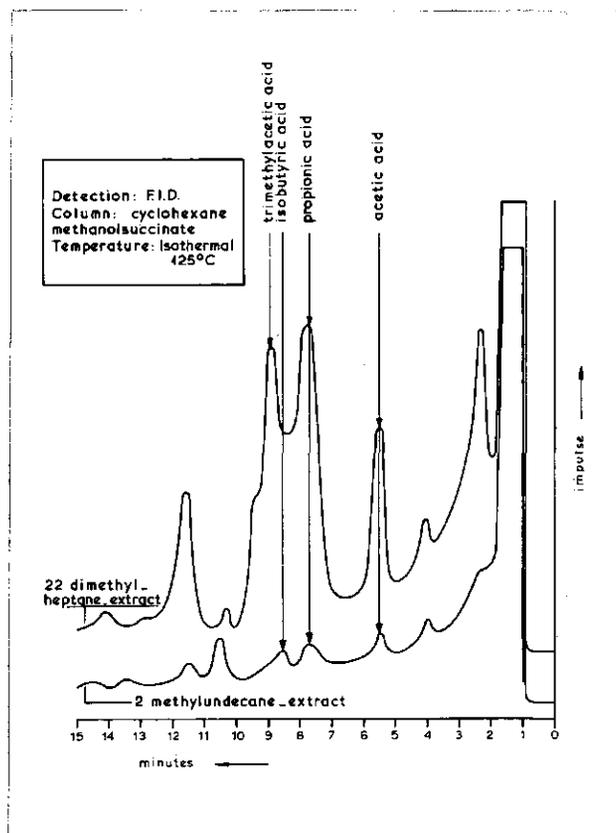


Figure 7 - Gaschromatograms of oxidation products of a *Pseudomonas* strain grown on two isoparaffins.

water by accumulation of  $\alpha$ -substituted fatty acids from oil degradation seems to be very unlikely.

#### Odorous metabolites, synthesized during microbial degradation of oil

Recent investigations in the USA on the origin and identity of very intense smelling substances in water have shown that certain Actinomycetes like *Streptomyces lavendulae* and *Streptomyces odorifer* synthesize earthy smelling compounds like geosmin (Medsker-Jenkins-Thomas, 1968; Rosen e.a., 1968) and 2-methylisoborneol (Medsker e.a., 1969; Rosen e.a., 1970). These two compounds are tertiary alcohols with a saturated ringsystem. For this reason they will have a relatively low biodegradability.

This characteristic and the very low TOC of about 0.1 ppb make these microbial products very meaningful as to the odour of drinking water.

Because the chemical structure of these earthy smelling compounds very much resembles that of cyclic paraffins a stimulating effect of water pollution by oil on the production of these substances by *Streptomyces* cannot be excluded a priori. A detail study on the influence of oil compounds, pH and other parameters on the production of these odorous metabolites by Actinomycetes is necessary.

Orientating experiments in our laboratory have shown already that a strong earthy odour is developed if a *Streptomyces lavendulae* strain is grown on a medium with iso-octane as only source of carbon, while no odour at all is developed when n-undecane is being used as carbon source. The research in this field will be continued.

#### Discussion

Odour compounds that are directly or indirectly introduced in the water by oil pollution can be constituents of the oil, intermediates of the microbial mineralization or can be synthesized during the microbiological utilization of hydrocarbons.

Sulfur compounds and several polycyclic aromates like indene and naphthalenes could be mainly responsible for the odour of oil products. Storage of water that is contaminated with these odour compounds may considerably improve its quality as a result of biological mineralization. A treatment consisting of ozonization followed by adsorption on activated carbon can be of interest. A general survey of the microbial oxidative degradation of hydrocarbons and the additional experiments on the odour intensity and the accumulation of iso-fatty acids showed that there is no clear evidence to assume that intermediate oxidation products of hydrocarbons have an important effect on the odour of surface water.

The possible stimulating effect of oil compounds on the production of earthy smelling substances by Actinomycetes has also been considered as it might adversely influence the odour of stored water or water that is filtered over an activated carbon bed.

Finally it should be remembered that oil pollution can reduce the water quality by odour synergism among the neutral components of the water.

Apart from purification aspects more detailed studies on earthy smelling metabolites and odour synergism are necessary to evaluate the potential hazards that are involved in pollution of drinking water resources by oil. These studies are needed even more to be able to prevent the introduction of those compounds in the water that mainly cause the odour problems.

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